Annual Report for Period: September 30, 1992 - September 29, 1993

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# FUNDAMENTAL STUDIES ON THE CORROSION BEHAVIOR OF WELDMENTS IN MARINE MICROBIAL ENVIRONMENTS

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OFFICE OF NAVAL RESEARCH

800 North Quincy Street

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Scientific Officer: Dr. A. John Sedriks





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THE UNIVERSITY OF TENNESSEE

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## ABSTRACT

During the first year of this project, comprehensive literature reviews were completed in the areas of (1) weldments employed in marine applications, (2) microbially influenced corrosion (MIC) in marine environments, and (3) MIC of weldments in marine environments. Specific weldment types covering a wide range of materials were selected for MIC evaluation. Laboratory MIC evaluations were initiated on a prototype weldment (as-welded 304L stainless steel base metal, 308L filler metal) in the crevice condition. Combinations of variables were employed to enhance MIC attack of the weldment during bacterial exposures, as compared to the corrosion observed during sterile control exposures. The variables included three different consortia of marine bacteria, different degrees of solution aeration, and different solution replacement rates (dilution rates) during continuous low-flow conditions. Unfortunately, little differentiation between the bacterial and sterile-control results have been obtained to date. When corrosion occurred, either in the bacterial or control experiments, it always occurred as general or pitting-type corrosion at crevice sites within the weld-modified (weld-metal/HAZ) surface area, never within the unaffected base-metal area. Corrosion-potential and solution-redox-potential measurements suggested that oxygen-concentration cells contributed to the sterile-control results, but due to the uniform and highly-deaerated condition at the bacterial specimen surfaces, did not contribute to the bacterial results. Thus, it is believed that our bacterial conditions did not replicate the more natural condition of a non-uniform biofilm with resultant oxygen-concentration cells acting to influence the initiation of localized corrosion. The laboratory procedures have been modified to more nearly replicate this natural condition. New MIC evaluations are currently underway.

Annual Technical Report

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## INTRODUCTION

This project involves fundamental studies on the corrosion behavior of weldments in marine microbial environments. Various aspects of microbially influenced corrosion (MIC) are being studied in order to gain a better understanding of the phenomenon. Laboratory testing will lead to a ranking of weldments representative of those found in actual marine applications, based on their resistances to MIC. The following report contains pertinent background information on the subject, laboratory procedures, and the results obtained thus far. Plans for future research are found in the latter portion of the report.

Microbially influenced corrosion (MIC) refers to the effect that microorganisms can have on the natural corrosion rates of materials. MIC has been cited as a significant contributor to systems and parts failures in various industries. Almost all metals and alloys are susceptible to some form of MIC, including iron, steels, stainless steels, nickel alloys, aluminum and its alloys, and copper and its alloys. Considering the time and money that MIC costs every year and the widespread nature of its attack, it is becoming increasingly important to gain a better understanding of factors related to MIC, and be able to apply that knowledge to real situations.

This project involves the corrosion behavior of weldments in marine microbial environments. Corrosion plays a serious role in the performance of pipelines, ships, and offshore structures, and can be affected by the actions of microorganisms. Various aspects of MIC are examined in order to gain a better understanding of the factors associated with MIC in the marine environment. A ranking of relative resistances to MIC for weldments of interest will be developed.

The first stage in the project was a comprehensive literature review of general MIC, marine MIC, MIC of weldments, and the corrosion behavior of materials in marine applications with respect to MIC. Several comprehensive reviews on MIC exist (1,2), containing general information about MIC, organisms and mechanisms involved, and the metals and alloys affected. Although the larger portion of information is not specific to marine conditions, the reviews do contain valuable information about general characteristics of MIC. It was important to review all information on the microorganisms and conditions that have been associated with MIC, and to be able to apply that information in laboratory testing.

Literature was also obtained relating to the materials and weldments most commonly used in marine applications. A tentative list of weldments was formulated that represents a wide variety of weldments used in service (Table 1). These will be fabricated and tested further into the project.

## Background Information

Microorganisms are ubiquitous in aqueous environments. In these systems, nutrients are often scarce. When surfaces ( e.g., metal/alloy surfaces) are present, they often have a nutrient concentration higher than the surrounding environment. After the metal surfaces adsorb a conditioning film, microorganisms attach and colonize. The community of microorganisms serves to trap food, debris, and other microorganisms in the slime, or biofilm which then exists. Due to enhanced nutrient levels at surfaces, bacterial attachment is favored over planktonic growth. This biofilm tends to change the corrosion rates of materials under and around it. The microorganisms in the biofilm, and the biofilm itself, are able to affect the corrosion mechanisms on the metal surface in any of 5 ways: (1) by influencing the rates of anodic and cathodic reactions, (2) by changing the corrosion resistance through metabolism and metabolic products, (3) by producing corrosive metabolites, (4) by forming colonies or slimes that create differential aeration and concentration cells, and (5) by breaking down natural corrosion inhibitors and coatings (3).

Many factors influence the formation of the biofilm, including water chemistry, temperature, pressure, and mechanical effects (e.g., as related to flow vs. stagnation). Waters rich in nutrients lead to quickly formed, thick biofilms, while in waters with low nutrient amounts, biofilm formation is slow, and the resulting biofilm is thin (4). Surface roughness has been shown to be an important factor in fouling, with increased surface roughness leading to increased colonization. Generally, when failure is associated with MIC and welds are present, the weld areas show the greatest attack.

Table 1. Tentative list of weldments for evaluation.

Carbon and Low-Alloy Steels

1. HY-80
2. HY-100
3. HY-130
4. HSLA-80

Suitable consumables will be chosen depending on the welding process used.

Austenitic Stainless Steels

1. AISI 304L
2. AISI 316L
3. AISI 347

Consumables - 308, 316, 347

Copper Alloys

1. Phosphor Bronze (CDA 534) - ERCuSn-A (Filler)
2. High Silicon Bronze A (CDA 655) - ERCuSi-A (Filler)
3. 90-10 Cu-Ni (CDA 706) - ERCuNi (Filler)
4. 80-20 Cu-Ni (CDA 710) - ERCuNi (Filler)
5. 70-30 Cu-Ni (CDA 715) - ERCuNi (Filler)
6. Cu-Ni-Zn (65-18) (CDA 752) - ERCuNi (Filler)

Aluminum Alloys

1. 5052 - 5556 (Filler)
2. 5083 - 5556 (Filler)
3. 5086 - 5556 (Filler)
4. 5456 - 5556 (Filler)
5. 6061 - 4043/5556 (Filler)

Titanium Alloys

1. Ti-6Al-4V (ELI) - ERTi-6Al-4V(b) (Filler)
2. Ti-6Al-2Nb-1Ta-0,8Mo - ERTi-6Al-2Nb-iTa-IMo (Filler)
3. Unalloyed Ti (35A-100) - ERTi-1(b) (Filler)

Welding changes a number of variables in the metal, such as surface texture and solute distribution. Phase distributions change, and because of the temperature effects, grain size also changes. Localized melting, leading to solute enrichment at the exposed surface, as well as precipitates, inclusions, surface oxides, and residual stresses develop as a result of the welding process (5).

The biofilm community is diverse in nature. Generally, films are not continuous, instead showing discrete colonies of bacteria. The slime can serve as home to a variety of organisms. Many times under the influence of a biofilm, conditions are created underneath that cause anaerobic microenvironments for anaerobic bacteria (1). The community can function synergistically, with certain members providing conditions and functions necessary for the others to survive. Microorganisms within the biofilm are capable of creating an environment different than that of the bulk environment (pH, oxygen content, and organic and inorganic species). Thus, often times, corrosion occurs where it would not normally have been suspected.

As stated earlier, biofilms contain communities of bacteria, algae, food, debris and inorganics that can have a serious effect on the corrosion rates of metals and alloys in service applications. Certain organisms, such as algae and bacteria, have repeatedly been linked to biofouling. Able to survive in a range of conditions, algae can produce and consume oxygen. They form concentration cells and affect what can and can't get to the surface of the metals and alloys. They are able to produce food for other organisms and can lower pH, contributing to localized areas of corrosion.

Bacteria are a widely diverse group, a number of which are associated with the MIC mechanism. They are small, can survive in a variety of pH's, are able to live in various environments, and are able to use most organic substances as food. Bacteria can be aerobic (require oxygen), anaerobic (require deoxygenated conditions), or facultatively anaerobic (able to live in either type environment, but prefer oxygenated conditions). Certain bacteria have been repeatedly linked to MIC in both freshwater and marine environments.

The most cited occurrence of bacteria in conjunction with MIC is that of the sulfate-reducing bacteria (SRB) on iron. SRB are sessile in nature (6), thriving in colonies attached to surfaces. SRB can use sulfate ions as the terminal electron acceptor (oxidizing agent) for respiratory metabolism. Many SRB are able to produce hydrogenase, an enzyme that catalyzes the oxidation of cathodic $H_2$ which in turn leads to the reduction of sulfates by hydrogen ions, transferring energy to the organism (2). Sulfide reduced from sulfate reacts with hydrogen and iron ions to form $H_2S$ and FeS. $H_2S$ is known to be corrosive to irons and steels. When sulfates are present, SRB's

actively dominate. They are anaerobic, but can survive in seemingly aerobic environments, as long as they are provided with the anaerobic microenvironments they need (found under the biofilm).

Other bacteria have been linked to the MIC process. Iron oxidizing bacteria, such as *Gallionella*, *Sphaerotilus*, *Crenothrix*, and *Leptothrix*, can oxidize ferrous to ferric ions or manganous to manganic ions to obtain energy. They leave deposits, which create oxygen concentration cells. In addition, the metal ions cause local acidification through hydrolytic reactions and also cause an accumulation of chloride ions, creating an acidic chloride environment. Iron oxidizing bacteria are aerobes, preferring conditions with limited oxygen. Iron reducing bacteria include the Pseudomonads. They accelerate corrosion in mild steels and serve to shelter SRB. A sulfate oxidizing bacteria, *Thiobacillus thiooxidans*, which produces sulfuric acid ($H_2SO_4$) has also been cited in conjunction with MIC. *Cladosporium resinae* has been linked to MIC of aluminum alloys. Most references have been for fresh water cases, with limited references specific to marine MIC. However, much of the literature gives general information that can be carried over into marine applications.

In selecting a bacterial consortium, it was desired to have bacteria known to be linked to MIC. Under the guidance of the UTK Center for Environmental Biotechnology, several consortia were selected for use. These are given in Table 2.

Table 2. Bacterial consortia used in the experiments.

| Consortium A* | Consortium B | Consortium C** |
|---|---|---|
| - wild type<br>- known to contain SRB | - *Vibrio horveyi*<br>- *Vibrio natriegens*<br>- *Deleya marina* (wild type)<br>- 2 unknowns | - wild type<br>- known to contain algae<br>- known to contain SRB |

* A natural consortium from Newport News, VA coastal region.

** A natural consortium kindly supplied by Dr. Steve Dexter from the Lewes, DE coastal region.

**Experimental Description**

Since conditions that arise from a biofilm are similar to those of a crevice (oxygen depletion, acidification, and increased chloride concentration) a crevice geometry has been used throughout this experiment (Figure 1). Thus far, only the stainless steel weld prototype (304L base metal, 308L filler metal, full penetration, as-

welded condition) has been used. Coupons were held in place by an equal compression of the bolts on two low-halide silicone-rubber (GE RTV 664) rods. This produced a uniform crevice along the length of the weld coupon. No surface treatment was administered prior to tests.

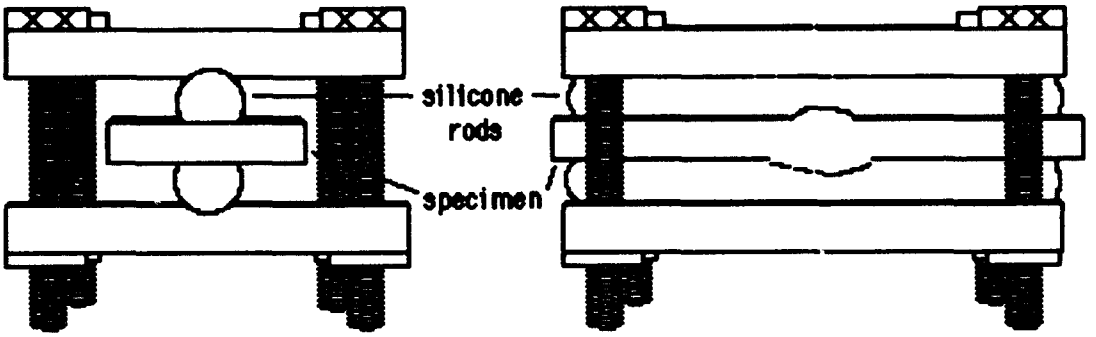


Figure 1. Crevice assembly used in experiments.

Each set of tests lasted two weeks. A variety of conditions has been used and a complete list is found in Table 3. In general, the bacterial cells contained a base medium of artificial seawater with added nutrients and were inoculated with a bacterial consortium. The control cells contained a base medium of artificial seawater, with or without added nutrients, but without the bacteria. Following the two-week exposures, test coupons were examined for evidence of MIC.

There are certain limitations to these laboratory tests. First, natural seawater, with its full spectrum of organisms is more corrosive than artificial sea water with fewer or different organisms (7,8). In general, biofilms do not have the well-documented effect on corrosion in marine environments that they do in fresh water environments (8). In addition, there are many variables related to the environment that the laboratory set-up does not take into account. Equilibrium values of oxygen are disturbed by the action of marine plants and organisms. Natural marine environments offer a more dynamic environment, subjected to physical disturbances and variable exposure to oxygen and nutrients (9). Unlike natural waters, temperature, aeration, nutrients, and flow conditions remained nominally constant during the laboratory exposures.

## PROCEDURES

Austenitic stainless steel weldments (as-welded 304L/308L), measuring 2.5 by 6.4 cm with the weld region centered on, and perpendicular to, the long dimension, were mounted in the crevice assembly shown in Figure 1 with a torque of 0.23 m-N (2 in-lb) applied to each bolt. Thus, the low-halide silicone-rubber rods (GE RTV 664) were compressed so that a uniform crevice was imparted along the length of the coupon. Two of these crevice assemblies were placed in each 2-liter test cell. Cells were sterilized at the UTK hospital with ethylene oxide gas.

The base medium used in the experiments consisted of artificial seawater, prepared under the guidelines of ASTM D1141 for substitute ocean water (minus Solution III), with and without nutrient additions. Nutrients were always added to the seawater used in the bacterial cells, but not always added to the seawater used in the control cells, as will be defined later. The nutrients consisted of yeast extract, sodium lactate and ascorbic acid. The resulting base medium, along with tubing to connect the test cells with the base-medium supply, were steam autoclaved for sterilization.

The sterile base medium was pumped into the test cells. After 1 mL of concentrated bacteria was grown for one day in 10 mL of the sterile solution with nutrients, this bacterial solution was aseptically injected into the bacterial cell and allowed to grow under batch (no-flow) conditions for 2 days (to promote biofilm formation). The control cell (no bacteria) also remained for 2 days under no-flow conditions. Flow was then started and a constant supply of sterile base medium was supplied to each cell at a predetermined dilution rate.

Tests were stopped 2 weeks after starting the constant flow through the cells. The cells were opened, open-circuit potentials of bright platinum were measured in the control and bacterial solutions, and corrosion potentials were measured for the control and bacterial test coupons. The crevice assemblies were disassembled and the coupons were photographed. Then, they were cleaned in a dilute nitric acid solution and examined for signs of corrosion. In some cases, the coupons were examined by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

Individual procedures are listed below. The experiments were modified from run-to-run in attempts to enhance the microbial corrosion effects, i.e., the differences observed in the results for the bacterial cells vs. the control cells (no bacteria). In these modifications, the bacterial consortium was of primary importance. The runs first involved bacterial consortium A, then B, then A + B, and finally C. The dilution rate,

i.e., the rate at which the base medium, including added nutrients, was supplied to the bacterial cell divided by the working solution volume in the cell, was also important with regard to bacterial effects. If the dilution rate is too low, insufficient nutrients are supplied to support bacterial growth on the specimen surface. If the dilution rate is too high, the planktonic bacteria in the solution are unduly "washed-out" of the cell, resulting in minimal attachment to the specimen surface. In the various runs, two dilution rates were employed, 10 and 30 vol. % / hour. A third modification involved aeration (oxygenation) of the cell electrolyte. Initially the cells were directly exposed to air through 0.2 μm filters; the purpose of the filters was to filter out air-borne bacteria, thus minimizing contamination of the cells. Therefore, the cells were naturally aerated. Later, the natural aeration was enhanced by directly and continuously sparging the cells with air. The presence of dissolved oxygen in the solution is, of course, a necessity for development of oxygen-concentration cells, i.e., cells developed by having oxygen available away from the crevice site for the cathodic reaction which in turn can support a high anodic reaction rate at the crevice site. The development of oxygen-concentration cells is thought to be a major effect in the MIC mechanism.

Run 1.

Run 1 employed consortium A for the bacterial cells, a 10 vol. % / hour dilution rate, with no air sparging (forced aeration) of the cells. The bacterial-cell medium consisted of seawater plus added nutrients of 1 g/L yeast extract, 0.1 g/L ascorbic acid, and 0.5 mL/L sodium lactate. The control-cell medium consisted of seawater with no added nutrients (to minimize the probability of air-borne bacterial contamination).

Run 2.

Run 2 employed either consortium B alone or a combination of A and B for the bacterial cells, a 10 vol. % / hour dilution rate, with no air sparging of the cells. The bacterial-cell and control-cell media were the same as in Run 1.

Run 3.

Run 3 employed a combination of A and B for the bacterial cells, and dilution rates of 10 and 30 vol. % / hour. The cells were sparged with air to enhance the development of oxygen-concentration cells. The control-cell and bacterial-cell media were the same; both contained added nutrients. Relative to previous experiments, the yeast content was divided by 10 (0.1 g/L); the other nutrient amounts remained the same.

Run 4.

Run 4 employed consortium C for the bacterial cell, a 30 vol. % / hour dilution rate, with air sparging of the cells. The control-cell and bacterial-cell media were the same as in Run 3. Following the tests, the coupons were examined with the SEM.

Run 5.

Run 5 employed consortium C for the bacterial cell, a dilution rate of 10 vol. % / hour, with air sparging of the cells. The control-cell and bacterial-cell base media were the same as in Runs 3 and 4.

Run 6.

Run 6 employed consortium C for the bacterial cell, a dilution rate of 10 vol. % / hour, with air sparging of the cells. The base medium for the cells was the same as in Runs 3, 4, and 5, except that 0.5 mL/L biocide (Kathon 886 MW, Rohm and Haas, Philadelphia, PA) was added to the control cell to reduce the probability of air-borne bacterial contamination.

## RESULTS AND DISCUSSION

In the descriptions of the corrosion observed on the control-cell or bacterial-cell weldment coupons, the following terms are used relative to specific locations: (1) the fusion zone (FZ) refers, of course, to the melted filler-metal/base-metal region which is covered by a high-temperature oxide (heat tint) produced by the welding process, and (2) the heat-affected zone (HAZ) refers to the rest of the weld-modified surface area, i.e., the surface regions on both sides of the fusion zone which also are covered by a high-temperature welding oxide. The results are given below and summarized in Table 3.

Run 1.

Run 1 did not give the results sought. Bacterial-cell coupons showed definite biofilm formation, but visual and microscopic examination failed to reveal any evidence of pitting or crevice corrosion. From the strong sulfide smell of the waste medium and upon dismantling the cells, it was evident that there was SRB activity. The control-cell coupons did show pitting corrosion at HAZ crevice locations. Corrosion potentials were approximately -280 mV (SHE) for the bacterial-cell coupons and ranged from +80 to

+112 mV (SHE) for the control-cell coupons. The platinum potential was lower in the bacterial solution.

Run 2.

Run 2 gave results similar to Run 1. The coupons exposed to only bacterial consortium B showed no biofilm formation, but those exposed to both A and B showed biofilm formation. Examination once again revealed no signs of pitting or crevice corrosion on any of the coupons exposed to the bacterial solutions, but pitting at HAZ crevice locations on the control-cell coupons. Corrosion potentials were in the same range as for Run 1 -- -249 to -289 mV (SHE) for the bacterial-cell coupons, +57 to +115 mV (SHE) for the control-cell coupons.

Run 3.

In this run, several of the variables in the experiment were changed. Dilution rates of 10 vol. % / hour and 30 vol. % / hour were used with a combination of bacterial consortium A and B. This was the first time that the control-cell and bacterial-cell media were the same (both contained the added nutrients). Also, this was the first time the cells were sparged with air. The bacterial-cell results improved, with a few small pits at HAZ crevice locations. There was SRB activity, indicated by the strong sulfide smell of the waste medium from the bacterial cells. The 10 vol. % / hour dilution rate appeared optimum. However, the control cell became contaminated with air-borne bacteria. No apparent corrosion was observed on the control-cell samples. Corrosion potential readings were still in the -260 mV (SHE) range for the bacterial-cell coupons. The corrosion potentials for the control-cell coupons decreased 200 mV into the range of -76 to -188 mV (SHE), which was probably due to the control cells becoming contaminated.

Run 4.

Run 4 employed a different bacterial consortium than had been used previously. Consortium C was used in conjunction with a 30 vol. % / hour dilution rate. The cells were sparged with air. The bacteria proved to be very active. A thick biofilm was formed in the first few days and the bacteria started to back up into the input tubing, and into the carboy that contained the sterile base-medium supply, within two days of starting the flow. The base-medium supply became contaminated. On replacing the supply, it again became contaminated. The control cell also became contaminated with air-borne bacteria within the first three days of testing. It was unknown if there was any SRB activity in the bacterial cell -- no sulfide smell was detected.

When examinations were conducted after the tests, small pits were found at HAZ and FZ crevice locations on one of the bacterial-cell coupons. Upon microscopic examination, there appeared to be preferential attack of one phase in the FZ pit. The pits were further examined by SEM with EDS analysis. Features associated with MIC in stainless steels were found -- higher chromium and chloride concentrations, and decreased iron concentrations in the pits. Since the pits were small, the tests showed nothing conclusive. The control-cell samples underwent general corrosion (not pitting) at FZ crevice locations. Corrosion potentials were in the range of -265 to -282 mV (SHE) for the bacterial-cell coupons and -9 to -32 mV (SHE) for the control-cell coupons. The platinum potential was considerably lower in the bacterial solution.

Run 5.

Run 5 gave the most promising results. Consortium C was used again in combination with a 10 vol. % / hour dilution rate. The cells were sparged with air. There was heavy biofilm formation on the coupons in the bacterial cell after the first two days. There also was a black corrosion product under the biofilm at the metal surface and a slight sulfide smell was detected, indicating that there was SRB activity. The control cell was contaminated with air-borne bacteria within the first 3 days of flow.

When the bacterial-cell coupons were examined after the tests were stopped, large pits were found at HAZ crevice locations and general corrosion was found at FZ crevice locations. The control-cell became contaminated. The control-cell coupons underwent corrosion, with general corrosion and pitting at FZ crevice locations. Corrosion potential readings were low for both cells, around -275 mV (SHE) for the bacterial-cell coupons and in the range of -197 to -236 mV (SHE) for the control-cell coupons. The platinum potential was considerably lower in the bacterial solution.

Run 6.

Run 6 attempted to duplicate the results obtained in Run 5 while introducing a biocide in the control cell to retard air-borne bacterial contamination. The same conditions were used as had been used in Run 5: 10 vol. % / hour dilution rate, air sparging, and consortium C in the bacterial cell.

There was biofilm formation on the bacterial-cell coupons, with black corrosion products under the biofilm adjacent to the metal surface. However, the biofilm was not as thick as that in Run 5. There was a slight sulfide smell, indicating SRB activity was taking place. Examination showed no signs of corrosion on the bacterial-cell specimens. However, there was one large pit on each of the control-cell samples, at FZ crevice and

HAZ crevice locations, respectively. Corrosion potentials were -253 to -279 mV (SHE) for the bacterial-cell coupons and +95 to +103 mV (SHE) for the control-cell coupons. The platinum potential was considerably lower in the bacterial solution.

Table 3. Summary of Conditions and Results of Laboratory Testing.

| Cell (# of samples) | Medium | Bacterial Consor-tium | Dilution Rate (vol. % /hour) | Air Sparging | Platinum Potential (mV vs. SHE) | Corrosion Potential (mV vs. SHE) | Results |
|---|---|---|---|---|---|---|---|
| RUN 1 | | | | | | | |
| Control (2) | ASTM seawater | -- | 10 | NO | +41 | 1. +112<br>2. +80 | Pits at HAZ crevice locations. |
| Bacterial (2) | ASTM seawater + nutrients | A | 10 | NO | -109 | 1. -280<br>2. -278 | No apparent signs of corrosion. |
| RUN 2 | | | | | | | |
| Control (4) | ASTM seawater | -- | 10 | NO | -- | 1. +57<br>2. +98<br>3. +112<br>4. +115 | Pits at HAZ crevice locations. |
| Bacterial (2) | ASTM seawater + nutrients | B | 10 | NO | -113 | 1. -249<br>2. -249 | No apparent signs of corrosion. |
| Bacterial (2) | ASTM seawater + nutrients | A+B | 10 | NO | -136 | 1. -279<br>2. -289 | No apparent signs of corrosion. |
| RUN 3 | | | | | | | |
| Control (2) | ASTM seawater + nutrients | -- | 30 | YES | -- | 1. -188<br>2. -76 | Contaminated.<br>No apparent signs of corrosion. |
| Bacterial (2) | ASTM seawater + nutrients | A+B | 30 | YES | -- | 1. -270<br>2. -242 | No apparent signs of corrosion. |
| Bacterial (2) | ASTM seawater + nutrients | A+B | 10 | YES | -- | 1. -262<br>2. -268 | Very small pits at HAZ crevice locations. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| RUN 4 | | | | | | | |
| Control (2) | ASTM seawater + nutrients | -- | 30 | YES | +261 | 1. -9<br>2. -32 | Contaminated. General corrosion at FZ crevice locations. |
| Bacterial (2) | ASTM seawater + nutrients | C | 30 | YES | -114 | 1. -265<br>2. -282 | Small pits at HAZ and FZ crevice locations. |
| RUN 5 | | | | | | | |
| Control (2) | ASTM seawater + nutrients | -- | 10 | YES | +281 | 1. -236<br>2. -197 | Contaminated. General corrosion and pitting at FZ crevice locations. |
| Bacterial (2) | ASTM seawater + nutrients | C | 10 | YES | -139 | 1. -272<br>2. -276 | General corrosion at FZ crevice locations. Pits at HAZ crevice locations. |
| RUN 6 | | | | | | | |
| Control (2) | ASTM seawater + nutrients + biocide | -- | 10 | YES | +288 | 1. +103<br>2. +95 | Large pits at HAZ and FZ crevice locations. |
| Bacterial (2) | ASTM seawater + nutrients | C | 10 | YES | -99 | 1. -253<br>2. -279 | No apparent signs of corrosion. |

In reviewing the overall results, it is noted that when corrosion of the weldment coupons occurred, either in the control or bacterial cells, it always occurred at crevice sites in the weld-modified surface regions (HAZ and/or FZ), never in the base-metal regions. Therefore, for the prototype 304L/308L stainless-steel weldment coupons, in the as-welded condition, the weld-modified surface regions are least resistant to crevice corrosion under the conditions of these experiments.

With regard to the effects of MIC, the key difficulty thus far has been finding a combination of bacteria, dilution rate, and aeration sufficiently aggressive to reproducibly attack the stainless steel weld prototype, chosen for its intermediate properties. Consortium B contained *Vibrio natriegens*, which has been cited to increase corrosion because of the extracellular polymer it forms. However, in the cells where only consortium B was used, there was little or no biofilm formation. The first two consortia (A and B) were not sufficiently aggressive under any of the conditions

employed. Only bacterial consortium C resulted in corrosion of the bacterial-cell weldment coupons. Consortium C was a natural seawater consortium and contained a wide variety of organisms, including algae, SRB, and various other bacteria. However, when a sample was characterized by the UTK Center for Environmental Biotechnology to determine what had grown in the laboratory sample as compared to what was supposed to grow, results differed. The laboratory sample showed no signs of the algae or the SRB that had been in the original sample. There was however, a large gram-positive population, indicating that a great many other bacteria were present.

For the various control-cell runs, when the nutrients were added to the sterile base medium, the control cells always became contaminated with air-borne bacteria within the two-week exposures. This contamination occurred in spite of many precautionary measures. The only exception was when a biocide also was added to the sterile base-medium-plus-nutrients solution. Once contaminated, of course, the control cells no longer represented sterile control experiments. Since the best control-cell solution should consist of the base medium plus nutrients, i.e., exactly the same as the bacterial-cell solution minus the inoculated bacterial consortium, more work needs to be done in maintaining control-cell sterility. If a biocide addition is necessary, the possible effects of the biocide on corrosion must be clearly defined.

The major difficulty with the experiments to date is the inadequate differentiation between the control-cell and bacterial-cell results. In fact, overall, there has been as much or more corrosion produced by the control solutions (no bacteria intentionally added) than the bacterial solutions (even with the most aggressive bacterial consortium C). Several reasons are believed to have contributed to the results. First, for the seawater environment, the crevice geometry is believed to be an imposed condition too severe to allow discrimination of the MIC effects, i.e., even the control experiments produced general or pitting-type crevice corrosion within the two-week exposure time. The second reason involves relative aeration effects. It is noted that both the corrosion potentials and platinum potentials (solution redox potentials) were considerably higher in the control-cell experiments (when not contaminated by air-borne bacteria) than in the bacterial-cell experiments. This result suggests that the control-cell solutions were sufficiently aerated, but that the bacterial-cell solutions at the specimen surfaces were highly deaerated due to the metabolic actions of the bacterial consortia in the biofilms. Thus, oxygen-concentration cells could drive the crevice corrosion in the control cells but not in the bacterial cells. For the bacterial cells, we believe that this lack of dissolved oxygen over the entire small-specimen surface (due to a nutrient-rich medium, a high concentration of bacteria, and a resulting uniform biofilm -- all intended to accelerate the

MIC process) does not represent a normal, natural condition where large regions of a structure would contain little or no biofilm and would therefore constitute a large cathodic surface for oxygen reduction, thereby driving corrosion under deaerated biofilm deposits.

Based on the above tentative conclusions, the experimental procedures are being redesigned. Initial experiments are underway with the following sequential steps: (1) the corrosion potential of the weldment coupon (with no crevice geometry) in the air-sparged sterile base medium is monitored with time until a steady-state value is obtained (2 days), (2) the solution is then inoculated with bacterial consortium C while the corrosion potential continues to be monitored, (3) after the potential has decreased to a low steady-state value (2 days), representing biofilm formation and deaeration at the specimen surface, the potential of the specimen is potentiostatically increased to its initial value (the no-bacteria, aerated value), and (4) while under potentiostatic potential control, the external current is monitored -- if localized corrosion initiates, the current will rise from its low passive value. This sequence of steps will replicate the situation whereby non-uniform biofilms are naturally produced on alloy surfaces, creating differential aeration cells as well as differences in electrolyte chemistry. Control experiments will be conducted in exactly the same way, but without the inoculation of bacteria.

## SUMMARY AND CONCLUSIONS

Comprehensive literature reviews have been completed on weldments employed in marine applications, marine MIC, and MIC of weldments in marine environments. A tentative list of weldments selected for evaluation in this study has been formulated.

MIC is a complex process, involving many variables. Several combinations of these variables have been employed in attempts to obtain conditions sufficiently aggressive to achieve MIC attack of prototype 304L/308L weldment coupons in the laboratory. A crevice geometry was employed in bacterial tests, and for comparison, in sterile control tests. In the bacterial tests, a number of different marine bacterial consortia were evaluated under conditions of different degrees of aeration and different dilution rates. A combination of bacterial consortium C, air sparging, and a 10 vol. % / hour dilution rate proved to be most aggressive in initiating corrosion. However, the sterile control tests also generally initiated corrosion in the same time frame. In both the bacterial and control solutions, when corrosion was initiated it was always located at crevice sites in the weld-modified surface regions (heat-affected zone or fusion zone),

never in the unmodified base-metal regions. Because of the inadequate differentiation between the bacterial and control tests, it is concluded that, at the present time, conclusive and reproducible MIC attack in the laboratory has not been achieved. However, reasons for this result have been tentatively identified and new tests with revised procedures have been initiated. The crevice geometry is believed to be a condition too severe in the seawater-based medium to allow differentiation of MIC; therefore, the new procedures do not employ the crevice geometry. Corrosion-potential and platinum-potential measurements in the experiments to date suggest that whereas the dissolved oxygen concentration was high in the sterile control tests, it was extremely low in the bacterial tests (due to a relatively small sample size, a rich-nutrient medium, uniform biofilm coverage of the sample, and the metabolic activities of the bacteria). Thus, it is believed that the bacterial tests to date did not adequately simulate the more natural condition of non-uniform biofilm deposits with accompanying development of oxygen-concentration cells which are important in initiating localized corrosion. The revised procedures are designed to replicate the more-natural biofilm conditions by potentiostatic application to the bacterial samples (uniform, deoxygenated biofilm) of potentials corresponding to the highly oxygenated condition. These new tests are currently underway.

## FUTURE RESEARCH

Currently, laboratory MIC evaluations are being conducted on the stainless steel prototype weld under new, revised experimental procedures. Once successful in this stage, the next step will be to perform similar tests on the formulated list of weldments found in Table 1 in order to evaluate their susceptibilities to MIC. Evaluations also will concentrate on the materials and microbial aspects associated with MIC. Materials will undergo corrosion characterization in an abiotic medium in order to study the nature of weldment zones and base-metal regions and their correlations to MIC attack. Regions most susceptible to MIC will be further evaluated. The microbial aspects of MIC will be further studied. Analyses will be performed on the microorganisms present at specimen surfaces, and the chemical species produced by these microorganisms, to further add to the understanding of MIC. The influence of weld fabrication variables will be investigated to determine if the performance of specific welds can be improved.

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